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Swelling of EPDM rubbers for oil-well applications as influenced by medium composition and temperature Part I. Literature and theoretical background

The paper describes the mechanism of interactions between hydrocarbon solvents and vulcanized rubber (representing crosslinked network structure). The problem is discussed from the point of view of thermodynamic principles of swelling, temperature and material factors affecting swelling of filled rubber vulcanizates, as well as the impact of swelling on properties of the materials. Special attention has been paid to the importance of models for the physical swelling of rubber in various hydrocarbons, which will provide a basis for prediction of swelling in their mixture like oils.

Key words: rubber, chemical structure, morphology, swelling, properties.

Wpływ składu oleju i temperatury na pęcznienie gumy EPDM do zastosowań w szybach naftowych Cz. I. Przegląd literaturowy i podstawy teoretyczne

W artykule opisano mechanizm oddziaływania między rozpuszczalnikami węglowodorowymi a usieciowanym kauczukiem (reprezentującym usieciowaną strukturę przestrzenną). Zagadnienie zostało przedyskutowane z punktu widzenia podstawowych praw termodynamiki dotyczących rozpuszczalności, temperatury i czynników materiałowych, mających wpływ na oddziaływanie rozpuszczalników na napełnione wulkanizaty oraz wpływu na ich właściwości. Ze względu na możliwość stworzenia podstaw do przewidywania zachowania się materiałów w mieszaninie rozpuszczalników, odpowiadającej olejom, szczególną uwagę poświęcono modelom opisującym fizyczne pęcznienie gumy w różnych węglowodorach.

Słowa kluczowe: guma, budowa chemiczna, morfologia, pęcznienie, właściwości.

1. Introduction

This is a first manuscript of a series covering the use of EPDM Rubbers for swelling applications in oil-well packers.

For many applications in the oil industry, equipment manufacturers spend much effort and investments to develop rubbers that give little swelling when

exposed to oil or water. The swelling phenomenon is not desirable in rubber manufacturing in general, but in oil field completion applications this behavior is turned into a necessity. Experimental measurements are the best options to determine sorption of swelling agents in polymers. However, they are time consuming and expensive so it is required to create faster ways to determine swelling behavior.

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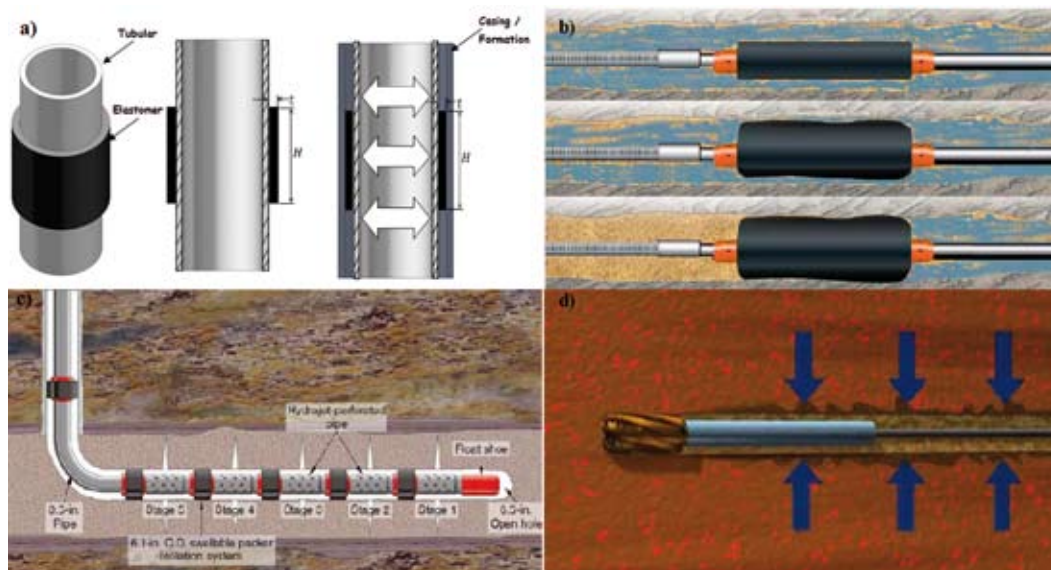


Figure 1. a) Schematic of a typical swellable packer; b) elastomer swelling creates zonal isolation; c) hydra-jet perforation system; d) underbalanced drilling [2]

Rys. 1. a) Schemat ilustrujący działanie typowego wypełnienia elastomerowego; b) pęczniejący elastomer zapewniający izolację strefową; c) wodno-strumieniowy układ do perforacji; d) niewyważone wiercenie [2]

Vulcanized elastomers have two properties distinguishing them from most other typical solids: they may absorb large amounts of solvent without dissolving, and they may undergo large deformations with correspondingly small stresses [1]. Due to exposure to different chemical substances, the properties of elastomers undergo changes. One of the most common effects is physical swelling due to the presence of the crosslinked network structure. Depending on the base elastomer and the swelling liquid, the degree of swelling varies from negligible or slight to quite large degrees of swelling of a few hundred percent. 100% of swelling means a weight increase of the rubber sample by 100%. The swelling fluids interact with chemical ingredients contained in the elastomers and thus influence the mechanical or processing properties of the elastomer. Swelling of elastomers can be used for simple volume-increase or for functional effects such as self-healing. Elastomers exhibit a dynamic change in volume and thickness when exposed to a swelling medium: water, oil or acids/bases [2].

Swelling of elastomers is in general undesirable. However, because elastomers can swell in a controlled way to different degrees in selective fluids, this effect can also be used in some industrial applications; for example as swellable seals which are successfully employed for enhanced oil recovery through relatively low-cost, yet long-term and effective fluid shutoff, underbalanced drilling, sand screens, cement-less seals, zonal isolation etc. as shown in Figure 1 [2–4].

A packer is a mechanical sealing device used down-hole in the oil-well to block the flow of fluids through the

annular space between the drill-pipe and the wall of the hole. The packer consists of a tubing string surrounded by the packing seal element: a rubber component that mechanically expands to block the annular space and to allow fluids to flow only through the encased tubing. Packers are classified according to their function, configuration, and method of setting. Some mechanical packers are designed to be retrievable from the hole and reconditioned for multiple uses [5].

Swelling seals can be divided for 3 types:

1. Water swelling – able to swell in water vapor, where swell time and volume is dependent on temperature and water salinity; swell rate is faster at higher temperatures and lower salinities;
2. Oil swelling – swelling occurs by a diffusion-absorption process in condensate and gas; swell time and volume is governed by temperature and hydrocarbons composition; swell rate is faster at higher temperature and in lighter hydrocarbons;
3. Hybrid swelling – combinations of elastomers capable of swelling in either hydrocarbon or water based solutions [6].

Water-swelling elastomers work on the principle of a diffusion gradient, a process that encourages the movement of water molecules across a gradient, where there is a salinity difference on either side of the gradient. Oil-swelling elastomers work on the principle of absorption and dissolution. The swelling rate and volume increases are directly related to the composition and characteristics of the oil. The specific gravity of the oil plays an important role, but other qualities of the oil can also affect swelling behavior [5, 7].

The rubber seal is wrapped on the pipe with weight, grade and connection specified by the hole construction (Figures 1a and 1b). The seal length is determined by the required differential pressure, the well temperature and application. Solid metal end rings are attached to the base pipe and guide the elastomer into the correct position in the well. Critical to the function of the end rings is that they help to focus the sealing forces generated by the swelling of the elastomer. The end rings support the elastomer, which results in a hydraulic annular seal. Swellable packers can have pressure ratings as high as 68,95 MPa (10 000 psi) [8]. Swelling seals are used successfully because of their ease of design and manufacture, simplified running into wells, spacing out and setting especially when large numbers of seals are required, the ability to conform to uneven open hole well surfaces and low costs when compared to conventional mechanical packers.

2. Objective of the study

The goal of the present study is to create a way of predicting the equilibrium swelling of EPDM rubber as a function of temperature and swelling medium composition for the purpose of oil-well applications. The interaction between hydrocarbon solvents with the crosslinked network structures (vulcanized rubber) at higher temperatures is the basis of these studies. By using theoretical literature it is possible to predict the maximum degree of swelling of EPDM rubber in selected components of crude oil at room temperature. The challenge is to find correlations for the swelling at higher temperatures. By swelling measurements in a well-known medium, it is possible to deduct general rules to correlate these to the crude oil compositions. The main purpose is then the derivation of a model for the physical swelling of EPDM rubber in various hydrocarbons, which will provide a basis for prediction of the swelling of this elastomer in a pure organic solvent as well as in a mixture of various components like in oils.

3. Theory

3.1. Mechanism of solvent-swelling of a packer

Water-swelling elastomers swell through the absorption of saline water following the mechanism of osmosis, while oil-swelling elastomers swell by the absorption of hydrocarbons through a diffusion process [2, 9]. The mechanism of swelling can be illustrated like in Figure 2 as a combination of three separate processes, i.e.:

1. Solvent absorption at the polymer surface;
2. Solvent penetration into the polymer, firstly by occupying the pores and free volume and then the solvent molecules diffusion into the polymer;
3. The polymer structure expands as the solvent trapped in the pores penetrates into the network of the polymer chains to swell them [10].

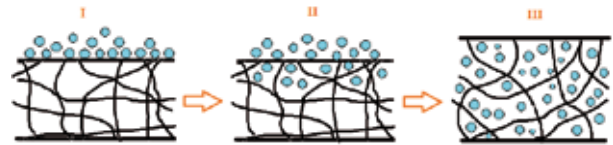


Figure 2. Absorption of hydrocarbons by elastomer through a diffusion process

Rys. 2. Absorpcja węglowodorów przez elastomer w wyniku procesu dyfuzji

For the elastomer wrapped on a piece of pipe, like in swelling packers systems (Figure 3a), the result is an increase of the manufactured outside diameter of the swellable elastomer. When the polymer is immersed in a liquid with similar solubility parameter (see later), a strong affinity between polymer and liquid happens. The result is that the packer will swell in some cases to several 100% by volume. Oil continues to diffuse into the elastomer causing the packing element to swell until it reaches the inside diameter of the open hole

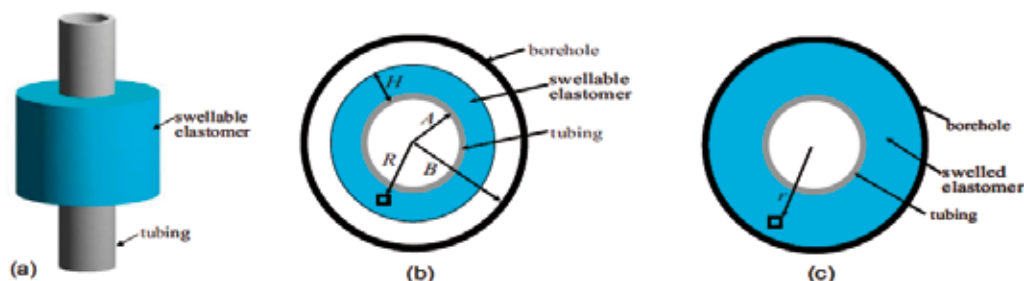


Figure 3. a) A packer consists of an elastomer crosslinked around the exterior surface of a metallic tubing; b) when the elastomer is dry, the radius of the packer is smaller than that of the borehole; c) as the solvent migrates into the elastomer, the elastomer swells to the size of the borehole [7]

Rys. 3. a) Wypełnienie złożone z usieciowanego elastomeru umieszczonego wokół zewnętrznej powierzchni metalowej rury; b) kiedy elastomer jest „suchy”, promień wypełnienia jest mniejszy niż wewnętrzny promień odwiertu; c) w momencie kontaktu z rozpuszczalnikiem elastomer pęcznieje, całkowicie wypełniając obszar odwiertu [7]

(Figure 3c). The swelling continues until the internal stresses inside the elastomer reach equilibrium: the net effect of the mechanical limitations by the configuration of the packer in the well, the internal pressure created in the rubber by the absorbed solvent and the restoring forces due to the expansion of the crosslinked three-dimensional network. When swelling reaches an equilibrium, the mechanical properties and volume remain constant. The swell pressure increases until diffusion can no longer occur. At this point a differentially sealing annular barrier is created. If further expansion after equilibrium is reached it will be due to thermal chain degradation of the polymer [8].

3.2. Thermodynamic principles of swelling

When the thermodynamic properties of oil and rubber polymer are similar, the attraction between their molecules causes the swelling. The elastomer swells as a result of an entropy difference between the elastomer and the environment in which it is being used. This entropy disparity manifests itself in an effort to achieve an energy balance by creating a diffusion gradient between the elastomer and the surrounding fluid.

Vulcanized rubbers having a three-dimensional network incapable of dissolving completely, may nonetheless absorb a large quantity of a suitable liquid. For such a material, it is necessary to take into account the free energy of dilution and the configurational entropy of the network [11]. By the increased volume of the rubber throughout which the solvent may spread, there is an opportunity for an increase in entropy. This mixing tendency, expressed as the entropy of dilution (see next paragraph), may be expanded or reduced by the heat of dilution, ΔH , or first neighbor interaction free energy, ΔG .

If the free energy of mixing is negative, the rubber polymer and solvent may mix spontaneously. If it is positive, two phases are formed and the rubber polymer does not swell appreciably in the solvent. As the network is swollen by absorption of the solvent, the chains between network junctions have to assume elongated configurations, and a force similar to the elastic retractive force in rubber consequently develops in opposition to the swelling process. This force increases and the diluting force decreases in the course of swelling. Finally, these two forces are in balance and equilibrium swelling is reached [12]. Consequently, this swelling equilibrium may be explained as an interdiffusion process involving the solvent molecules and the polymer chains, balanced by an elastic energy loss upon stretching of the polymer chains. The crosslinks constrain the movement and complete separation of the chains and dispersion is resisted, but the elastomer does swell when the solvent molecules diffuse

into the network and cause the chains to extend. This expansion is opposed by the tendency of the chains to curl up and, eventually, the equilibrium degree of swelling depends on the type of solvent and the crosslink density; i.e., the higher the crosslink density, the lower the degree of swelling.

3.3. Swelling equilibrium: the Flory–Rehner equation

The equilibrium of a polymer-liquid system is determined by the condition that its free energy shall be a minimum with respect to changes in the composition of the mixed phases. Therefore, in the case when the mixed phases are polymer and a pure liquid, this means that the change in free energy resulting from the transfer of a small quantity of liquid from the pure liquid phase to the mixed phase shall be zero. In order to approach this quantitatively it is common to use the Gibbs free energy ΔG , defined as the change in the Gibbs free energy of the system due to the transfer of an unit quantity (1 mol) of liquid from the liquid phase to a very large quantity of the mixed phase [11]. The condition for equilibrium with respect to the transfer of liquid in a system at constant pressure is then:

$$\Delta G = 0 \quad (1)$$

The total free energy change can be expressed in terms of the heat of dilution ΔH and the entropy of dilution ΔS . Thus:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Frenkel [13] was the first to attempt to create a criterion for equilibrium swelling on the basis of a rough calculation of the swelling limit for vulcanized rubber. If the skeletal crosslinked structure is not broken by the action of the solvent, a state of equilibrium swelling may be achieved. The polymer in the network is progressively expanded because solvent is absorbed. The chains connecting multifunctional network junction points are forced to assume more elongated, less probable, configurations. Therefore, a decline in chain configurational entropy is produced by swelling. Contrary to this, a growth in entropy of mixing of the solvent with the polymer assists swelling. Neglecting effects of the heat of mixing of solvent and polymer, the entropy of chain configuration and the osmotic or mixing entropy become equal in magnitude and equilibrium will be obtained when these entropies balance each other.

This criterion was later developed by Flory and Rehner [14] into a general theory. This theory considers forces arising from three sources:

1. Mixing polymer and solvent changes the entropy; this entropy change is positive and promotes swelling;
2. The entropy change caused by reduction in numbers of possible chain conformations on swelling is negative and stands against swelling;
3. The heat of mixing of polymer and solvent may be positive, negative or zero – usually is slightly positive and opposes mixing [15].

Frenkel, Flory and Rehner [13, 14] assumed that the free energy of mixing and the elastic free energy in the swollen networks are additive. These are the free energy of mixing, ΔG_m , and the free energy of elastic deformation, ΔG_{el} . Thus, the free energy change concomitant with the absorption of a diluent was assumed to be given by:

$$\Delta G = \Delta G_m + \Delta G_{el} \quad (3)$$

Flory and Huggins [16] argued that for systems with polymer chains without crosslinks, to calculate the term ΔG_m , the dimensionless interaction parameter (χ) could be used, which is a measure of the compatibility between the polymer and the liquid:

$$\Delta G_m = RT(n_s \ln v_s + n_r \ln v_r + \chi n_s v_r) \quad (4)$$

The parameters n_s and v_s give the number of solvent molecules and the volume fraction of solvent, and the parameters n_r and v_r give the number of polymer molecules and the volume fraction of the polymer, R is the gas constant and T is the absolute temperature. The term $n_s \ln v_s$ is a measure of the disorder of solvent molecules in the liquid, and $n_r \ln v_r$ indicates the disorder of the chains in polymer. By assuming that there are no loose polymer chains in the network, the statistical thermodynamic model can be simplified to eliminate the term which is very small.

Considering the free elastic energy as a function of the number of active chains in the network and the volume fraction of polymer in swollen state ΔG_{el} can be used as a measure of the stretching that the network has undergone:

$$\Delta G_{el} = \left(\frac{RTv_e}{2} \right) \left[3v_r^{3/2} - 3 - \ln(v_r^{-1}) \right] \quad (5)$$

where v_e is a number of elastically active chains per unit volume – also often simply called the crosslink density – and v_r is the volume fraction of polymer in the swollen mass.

The Flory swelling model [17] now expresses the swelling equilibrium to consist of the sum of the Gibbs free energy changes of the solvent in the bulk phase and the elastic deformation of the polymer network. This equation can be also used to determine the chemical potential changes. One term in the equation is associated with a chemical potential change due to mixing, and the other term is relevant to elastic deformation induced by expansion of the network structure. When crosslinked

polymers are swollen in mixed solvents at constant temperature and pressure, the relation between the change of chemical potential and the Gibbs free energy for each component of the mix could be thermodynamically represented as follows:

$$(\mu_1 - \mu_1^0) = (\mu_1 - \mu_1^0)_{\text{mix}} + (\mu_1 - \mu_1^0)_{\text{el}} \quad (6)$$

where $(\mu_1 - \mu_1^0)$ is the chemical potential difference between the vulcanizate solvent system and the pure solvent, respectively. At swelling equilibrium $(\mu_1 - \mu_1^0)$ vanishes and Equation (6) becomes:

$$(\mu_1 - \mu_1^0)_{\text{mix}} = -(\mu_1 - \mu_1^0)_{\text{el}} \quad (7)$$

Then, the expression for the mixing term of component 1 is the Flory–Huggins equation:

$$(\mu_1 - \mu_1^0)_{\text{mix}} = RT \left[\ln(1 - v_r) - v_r + \chi v_r^2 \right] \quad (8)$$

where χ is the Flory–Huggins free energy parameter.

The Flory–Rehner equation in modified form may now be written as:

$$-\left[\ln(1 - v_r) - v_r + \chi v_r^2 \right] = V_s v_e \left[v_r^{1/3} - \frac{v_r}{2} \right] \quad (9)$$

where V_s is the molar volume of the solvent.

Molar volumes V_s can be found in literature, the volume fraction of polymer in swollen mass v_r is easy to determine experimentally:

$$v_r = \frac{1}{1 + Q} \quad (10)$$

$$Q = \left[\frac{(m - m_0)}{m_0} \right] \frac{d_2}{d_1} \quad (11)$$

where Q is the coefficient of swelling, m_0 and m are specimen weights before and after immersion in the solvent, d_1 and d_2 are the densities of the solvent and the unswollen vulcanizate, respectively [18].

3.4. Solubility parameter

The solubility parameter (δ) is a basic property of all materials, and is often employed to describe the compatibility between polymers and liquids. It is defined as the square root of cohesive energy density CED:

$$\delta = (CED)^{1/2} = \left(\frac{E_{\text{coh}}}{V_s} \right)^{1/2} = \left(\frac{\Delta H - RT}{V_s} \right)^{1/2} \quad (12)$$

where ΔH is the enthalpy of evaporation, V_s is the molar volume, R is the gas constant and T is the absolute temperature. Equation (12) indicates that the cohesive energy relates to the heat of vaporization, which is experimentally accessible. The degree of swelling can be estimated for a respective liquid-rubber combination, if the solubility parameters for both substances are well known.

If the square root of the difference between the solubility parameters of the rubber and the solvent is less than one $[(\delta_r - \delta_s)^{1/2} < 1]$, then the rubber will swell significantly in the solvent. That means the closer the values of solubility parameters (the smaller $\Delta\delta$) of solvent and rubber, the better the compatibility. When a fluid consists of two or more fractions, determination of the solubility parameter can be difficult [19]. The solubility parameters for most solvents and rubbers/polymers have been determined by experiment, and respective values can be found in literature. For the case of the main polymer EPDM involved in this study, Brandt-Nielsen and Hansen [20] reported that the molecular weight and the degree of branching of EPDM do not have a significant effect on the solubility parameter, so it can be assumed the value of this parameter is constant.

To estimate the solubility parameters at higher temperatures, the following Equations (13) and (14) are used to for liquids and rubbers above their glass transition temperature, respectively:

$$\ln \delta^T = \ln \delta_{298} - 1,25\alpha(T - 298) \quad (13)$$

$$\ln \delta^T = \ln \delta_{298} - \alpha(T - 298) \quad (14)$$

where α is the coefficient of linear thermal expansion of the oils and rubbers [12]: for EPDM it is $1.6 \cdot 10^{-4} \text{ [K}^{-1}\text{]}$, where addition of fillers reduces this value slightly.

The term solubility parameter was first used by Hildebrand and Scott: Equation (12). A widely used solubility parameter approach to predict polymer solubility is that proposed by Hansen [21]. The basis of these so-called Hansen solubility parameters (HSP) is that the total energy of vaporization of a liquid consists of several individual parts. These arise from atomic dispersion forces E_D , molecular permanent dipole-dipole forces E_P , and molecular hydrogen bonding: electron exchange E_H . The total cohesion energy E is the sum of the individual energies:

$$E = E_D + E_P + E_H \quad (15)$$

Dividing this by the molar volume V gives the cohesion energy density. This is identical to the square of the total (Hildebrand) solubility parameter δ and consequently is the sum of the squares of the Hansen D, P, and H components:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (16)$$

where δ_D , δ_P , and δ_H are the components for the dispersive, polar, and hydrogen bonding interactions, respectively. The SI unit for the solubility parameter is $\text{MPa}^{1/2}$.

The gas-phase dipole moment is not temperature dependent, although the volume of a liquid does change with temperature, what changes its cohesive energy

density. The change of the δ_D , δ_P , and δ_H parameters for liquids with temperature T can be estimated by the following equations:

$$\ln \delta_D^T = \ln \delta_D^{298} - 1,25\alpha(T - 298) \quad (17)$$

$$\ln \delta_P^T = \ln \delta_P^{298} - 0,5\alpha(T - 298) \quad (18)$$

$$\ln \delta_H^T = \ln \delta_H^{298} - (1,22 \cdot 10^{-3} + 0,5\alpha)(T - 298) \quad (19)$$

where δ_D^T , δ_P^T , and δ_H^T are the Hansen solubility parameters at absolute T , and α is the coefficient of thermal expansion [21]. Higher temperature means in general an increase in rate of solubility/diffusion/permeation and larger solubility parameters spheres. Solubility parameters decrease with increased temperature as shown in Equations (17–19). Increasing the temperature can cause a non-solvent to become a good solvent and vice versa. The hydrogen bonding parameter is the most sensitive to temperature, because as temperature increases, more and more hydrogen bonds are broken or weakened, so this parameter can decrease more rapidly than the others [21].

3.5. The Flory–Huggins parameter

The Flory–Huggins interaction parameter χ is a dimensionless quantity which is a function of the interaction energy characteristics of a given solvent-solute pair [16]. As mentioned previously, if the free energy of mixing is negative, the polymer and solvent may mix spontaneously to form a solution, and if it is positive, two phases form and the polymer does not dissolve appreciably in the solvent. For polymer solubility, the Flory–Huggins interaction parameter must be either negative or a small positive number. The maximum critical value of the Flory–Huggins parameter below which the polymer and solvent are miscible over the entire composition range is essentially given by $\chi \leq 0.5$.

In equation (8) χ is a free energy parameter which includes both entropy and enthalpy contributions:

$$\chi = \chi_S + \chi_H \quad (20)$$

The Flory–Huggins interaction parameter is interpreted as a residual free energy function rather than the original enthalpy parameter, thus it can be separated into enthalpic χ_H and entropic χ_S contributions. χ_S was found empirically for nonpolar systems to be equal to 0.34 [18]. The parameter χ_H is related to the heat of mixing of the polymer with the solvent. Combining of these approaches gives the following equation:

$$\chi \cong 0.34 + \frac{V_s(\delta_s - \delta_r)^2}{RT} \quad (21)$$

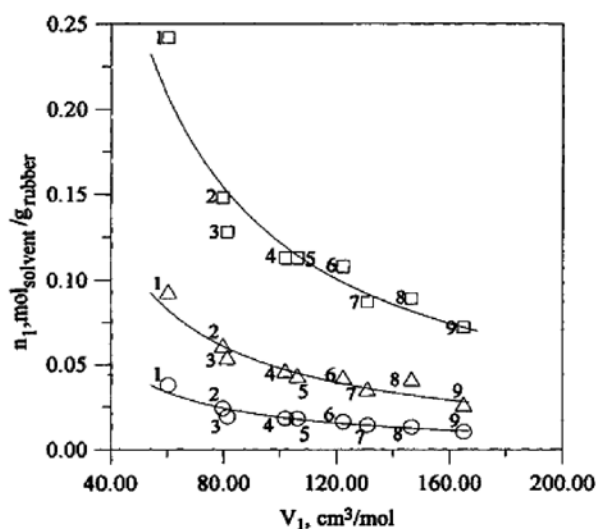
where δ_s and δ_r are the solubility parameters of solvent and polymer, respectively.

3.6. Molar volume of the swelling liquid

The deformation of vulcanizates caused by swelling as described by the Flory–Rehner equation indicates that the deformation depends on molar volume of the solvent and on the crosslink density. That part of the Flory–Rehner equation [14] which describes the change of the Gibbs free energy of mixing of the solvent and the

polymer, does not take into account crosslink density, although it is important when a polymer is connected in the network. Brandt-Nielsen and Hansen [20] found that for maximum swelling of crosslinked EPDM, the molecular volume was an important parameter that determined the number of moles taken up.

The correlation between the number of moles of solvent in a same sample, but for different organic solvents and molar volume of these solvents can be approximated by a decreasing power curve [1] (Figure 4). It shows that the difference in molar volumes of solvents mainly changes the number of neighboring molecules of solvent in a swollen gel and it is different from the number of the particular molecules in the pure state of solvents.



Liquid	v_2	n_1
<i>n</i> -hexane	0.151	0.050
<i>n</i> -heptane	0.123	0.057
benzene	0.196	0.054
toluene	0.135	0.070
<i>m</i> -xylene	0.136	0.060

Figure 4. Relationship between moles of the solvents in swollen gel, n_1 , at equilibrium swelling and molar volume of solvents V_1 ($= V_s$) for one EPDM samples with different molar mass of polymer segments between crosslinks, M_c (\square) 60568, (Δ) 26109 and (\circ) 4214; solvents: (1) CS_2 , (2) $CHCl_3$, (3) THF, (4) C_6H_6 , (5) MeC_6H_5 , (6) $Me_2C_6H_4$, (7) *n*-hexane, (8) *n*-heptane, (9) iso-octane; v_2 represents the volume fraction of vulcanizate

Rys. 4. Zależność między udziałem molowym rozpuszczalników w żelu elastomerowym w stanie spęcznienia równowagowego a objętością molową rozpuszczalników V_1 ($= V_s$) dla próbek wulkanizatów EPDM o różnej masie cząsteczkowej pomiędzy węzłami sieci przestrzennej, M_c (\square) 60568, (Δ) 26109 and (\circ) 4214; rozpuszczalniki: (1) CS_2 , (2) $CHCl_3$, (3) THF, (4) C_6H_6 , (5) MeC_6H_5 , (6) $Me_2C_6H_4$, (7) *n*-heksan, (8) *n*-heptan, (9) izooktan; v_2 odpowiada udziałowi objętościowemu wulkanizatu w żelu

Figure 4 shows curves which consist of a relationship between moles of the solvents with different polarity and interactions with the elastomer crosslinked to different degrees. However, the comparison creates unnecessary mistakes as the different Flory–Huggins interaction parameters for the various solvent–elastomer combinations are neglected. If comparing particular results of this investigation [1] taken from one group of liquids assumed to have more or less equal Flory–Huggins parameters, as shown in Figure 4, it is seen that the higher the molar volume of a liquid the smaller volume fraction of vulcanizate is obtained, what means that higher swelling is obtained.

3.7. Swelling in a mixture of liquids

If the cohesive energy and molecular volume of the liquid are known, the swelling power of such a liquid can be calculated approximately. When investigating mixtures of two liquids, it has to be considered that at the molecular level the molecules of a liquid are close together and therefore exert strong forces on each other, which lead to the formation of the latent heat of evaporation. That represents the work done in overcoming the mutual cohesive energy of the molecules. Different liquids do not

have the same molar latent heats so it should be noted that their molecules cohere with different energies, and this difference depends partly on the chemical nature of the molecules and partly on the way they pack together.

Oils are complex combinations of a variety of molecules and their mutual solubility depends on molecular structure and chemical composition, such as aromatic, naphthenic or paraffinic contents. The solubility parameters of oils can be taken as estimated values because they were calculated from only three main components, i.e. the aromatic, naphthenic and paraffinic carbons, but in practice oils consist of a multiplicity of different components such as polar or heterocyclic combinations [22]. One approach to the problem relates to statistical thermodynamics to describe the swelling of rubbers in a single liquid [23]. Gee extended the method to mixed liquids; from that work there are two primary conclusions:

1. From two liquids of equal molar volume, the one whose heat of mixing with the polymer is the smallest will be preferentially absorbed;
2. From two liquids whose heats of mixing with the rubber are identical, the one with the smaller molar volume will be absorbed.

Existing research suggests that this hypothesis is good for natural rubber, less so for synthetic rubbers [11].

From another point of view, binary solvents with different solubility parameters for solvent 1, δ_{s1} , and solvent 2, δ_{s2} , and polymer δ_r are considered. When a mixture of two solvents of variable composition have

solubility parameters (δ_{s1} and δ_{s2}) larger or smaller than the solubility parameter of the polymer ($\delta_{s2} > \delta_{s1} > \delta_r$ or $\delta_r > \delta_{s2} > \delta_{s1}$), then the solvents can be considered as a non-symmetric liquid. A symmetric liquid (SL) occurs when the polymer is mixed with two solvents, whose solubility parameter δ_{s1} is smaller and the parameter δ_{s2} of the other liquid is larger than the solubility parameter of the polymer δ_r . The dependence of equilibrium swelling on a non-symmetric liquid composition does not have a maximum in the correlation between equilibrium swelling and composition of the liquid phase [19], so research focused on swelling of crosslinked elastomers in synthetic liquids more reasonable.

The presence of a maximum in the curve of the polymer network equilibrium swelling and the composition of the liquid phase, characterizes swelling in symmetric liquids. When considering a symmetric liquid in combination with crosslinked ethylene-propylene elastomer ($\delta_r = 16.0 \text{ MPa}^{1/2}$) which was swollen to equilibrium at 25 °C in solvents of different polarity, it was observed, that with decrease in solubility parameter value of component 1 in the symmetric liquid ($\delta_{s1} < \delta_r$) the maximum value of equilibrium swelling, Q , shifted to the range of larger concentration of component 2 in the mixture. On the opposite side, with decrease in the solubility parameter δ_{s2} of component 2 ($\delta_{s2} > \delta_r$) the maximum Q represents the composition of the liquid phase enriched by component 1 (Figure 5) [24].

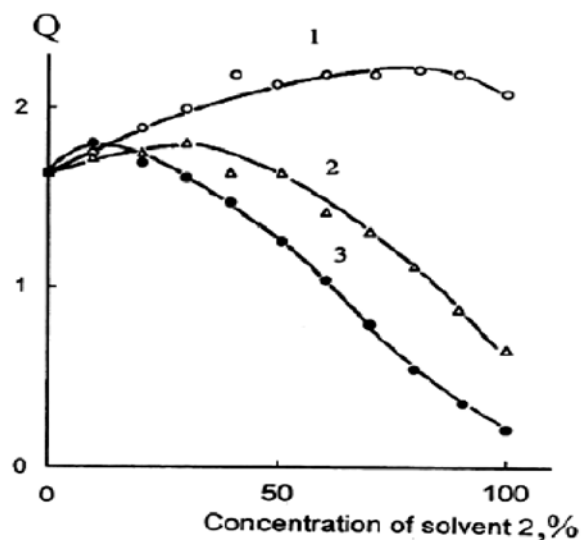


Figure 5. Dependence of equilibrium swelling of crosslinked elastomer EPDM on the concentration of component 2 in the mixtures heptane ($\delta_1 = 15.2 \text{ MPa}^{1/2}$) with: 1 – toluene ($\delta_2 = 18.2 \text{ MPa}^{1/2}$), 2 – amyl acetate ($\delta_2 = 17.3 \text{ MPa}^{1/2}$), 3 – ethyl acetate ($\delta_2 = 18.6 \text{ MPa}^{1/2}$) [24]

Rys. 5. Zależność wielkości pęcznienia równowagowego usieciowanego EPDM od zawartości składnika 2 w mieszaninach heptanu ($\delta_1 = 15.2 \text{ MPa}^{1/2}$): 1 – toluenem ($\delta_2 = 18.2 \text{ MPa}^{1/2}$), 2 – octanem amylu ($\delta_2 = 17.3 \text{ MPa}^{1/2}$), 3 – octanem etylu ($\delta_2 = 18.6 \text{ MPa}^{1/2}$) [24]

Neglecting the change of volume by mixing, the solubility parameter of the mixture of two liquids can be presented by:

$$\delta_{12} = v_{s1}\delta_{s1} + v_{s2}\delta_{s2} \quad (22)$$

where v_{s1} and v_{s2} are the volume fractions of components 1 and 2, and δ_{s1} and δ_{s2} are the solubility parameters of components 1 and 2 [19]. A more exact evaluation of the δ_{s12} value is possible if the experimental data of enthalpy of mixing ΔH of the components are taken into account:

$$\delta_{12} = \left(v_{s1}\delta_{s1}^2 + v_{s2}\delta_{s2}^2 + \frac{\Delta H}{V_{12}} \right)^{1/2} \quad (23)$$

With a change in the δ_{s1} and δ_{s2} parameters, the synthetic liquid composition has a maximum equilibrium swelling [19]. Summarizing, Equation (21) for a polymer in binary solvents can be expressed in the form:

$$\chi_{12r} \cong 0.34 + \frac{V_{12}(\delta_{12} - \delta_r)^2}{RT} \quad (24)$$

$$V_{12} = m_{s1}V_{s1} + m_{s2}V_{s2} \quad (25)$$

where V_{12} is molar volume of the mixture of the components 1 and 2, and m_{s1} and m_{s2} represent the molar fractions of components 1 and 2 in the solvent [24].

The calculation carried out by Tereshatov *et al.* [24] lead to the conclusion, that in a mixture of components, having similar molar volumes V_1 and V_2 , preferential adsorption of components is absent. However, if $V_1 < V_2$, preferential adsorption is promoted by the difference in parameters of interaction, when $\chi_{12} > \chi_{1r}$. The greater the χ_{12} value at $V_1 \neq V_2$, the more likely preferential adsorption will take place with all other parameters being equal.

3.8. Polymer effects on swelling

Swelling is correlated with solubility. The solubility of liquids in a polymer is dependent on numerous factors including the physical properties of the solvents (see before) but also the polymer's chemical structure, such as polarity, branching, molecular weight of the polymer chains, crystallinity and the presence of crosslinks and fillers [25]. The rate of swelling further depends on temperature, pressure, diffusion coefficient, fluid composition and penetrant size.

3.8.1. Polymer structure: molecular weight distribution and branching

For a given solvent, decreasing the molecular weight of the polymer will increase solubility, i.e. if a polymer is immersed in a good solvent, the low molecular weight chains will dissolve first. Dissolution can also be affected by its polydispersity, i.e. polydisperse samples dissolve about twice as fast as monodisperse ones of the same number average molecular weight. Branched polymer chains generally increase solubility, although the rate, at which this solubility occurs, depends on the particular type of branching. Chains containing long branches, cause dense entanglements making the penetration of the solvent molecules difficult. Therefore, the rate of dissolution in these cases becomes slower than for short branching, where mutual interaction between chains is practically non-existent [17].

3.8.2. Polarity

Chemical resistance of polymers to hydrocarbon oils is caused by polar groups which tend to provide resistance to swelling in a hydrocarbon liquid. These polar side groups usually include hetero atoms (from groups 15–17 in periodic table) that form covalent bonds with the carbon atoms in the polymer chain. The electron pair is displaced to the more electronegative atom; a slightly electronegative charge is induced onto the electronegative atom with a slightly positive around the carbon atom. This produces a dipole moment which usually provides oil resistance. The presence of multiple polar groups like in long-chain polymers, can shift or eliminate the dipole moments and thus reduce the polymer's oil resistance [25]. It also has to be taken into consideration that hydrogen bonding can be quite pronounced and has a major effect on the solubility of materials [26].

The degree of swelling of elastomers which can swell when exposed to hydrocarbon based fluids depends on the chemistry of the oil and the temperature at which the exposure occurs. As mentioned before, the presence of polar groups in composition is, first of all, a measure of the degree of swelling of the elastomeric material in hydrocarbon media. When there is a low degree of polarity in the polymer, the swelling in hydrocarbon media is stronger [26].

3.8.3. Crystallinity

In general, amorphous polymers like most elastomers do not show much resistance to solvents, so they are quite prone to swell in comparison with rigid or crystalline plastics. Crystalline regions in a polymer are very difficult to dissolve, because the crystallites are very resistant to diffusion into the network due to the close packing of the chains, so the solvent molecules cannot make their way into these crystalline regions to release

the macromolecules [25]. The influence of crystallinity of polymers is also linked to the impact of crosslinking and solubility. Crystallinity provides a measure of oil resistance by decreasing the ease with which a solvent molecule may enter into the polymeric network. The greater the crystallinity of a polymer, the lower the swelling.

3.8.4. Crosslink density

In case of crosslinked polymers, an additional parameter as crosslink density of the vulcanizate or crosslinked network will affect swelling. The space between crosslink intersections determines a specific volume which can accept molecules of solvent in the swelling process. Consequently, the volume between crosslinks depends on the density of crosslinks, and is also one of the limiting factors in the swelling of a vulcanizate [1]. A lower adsorption of fluid by the vulcanized polymer is related to the limited mobility of the original rubber molecules due to the formation of a three-dimensional network. It is known that crosslinking limits solubility by constraining (forming tie-points) the material, although not changing the polymer's inherent affinity for any given solvent [27]. An increase in the amount of chemical crosslinking agent causes the formation of a denser network of the polymer and reduces the chain length between crosslinks, which in turn reduces liquid adsorption. The space between crosslink junctions then determines the specific volume which can accept molecules

of solvent and thus interact with the solvent in the swelling process. As the amount of crosslink agent is increased there is a maximum in the solvent adsorption curve (Figure 6) [27]. When the crosslink density increases, the network becomes denser and the material becomes harder, which is not in favor of solvent adsorption. The solvent adsorption decreases with increasing crosslink agent content, so it is important to determine the optimum amount [27].

When comparing the effective and theoretical crosslink density, it is concluded that the double bonds in EPDM's third monomer units have participated in chemical crosslinking, and the physical crosslinks and entanglements weaken the chemical crosslinking effect [27]. The absorption by crosslinked polymers can be explained in terms of swelling as a diffusion phenomenon driven by the affinity of the molecules of the swelling material for the molecules of the contacting fluid. Wu and Zhou in their studies [27] showed that oil absorption by EPDM increases with the amount of EPDM in a blend of EPDM/4-tert-butylstyrene (tBS) at the beginning, what can be explained by the occurrence of some macromolecular and oleophilic soft monomers in the EPDM chain (tBS is a rigid monomer). Solvent absorption in this system reaches its maximum when the EPDM content is 60% vs. the tBS, because then the most relaxing three-dimensional network structure is obtained. When the content exceeds 60%, oil absorbency decreases as the 4-tert-butyl groups normally gives large cavities in the network due to its specific structure.

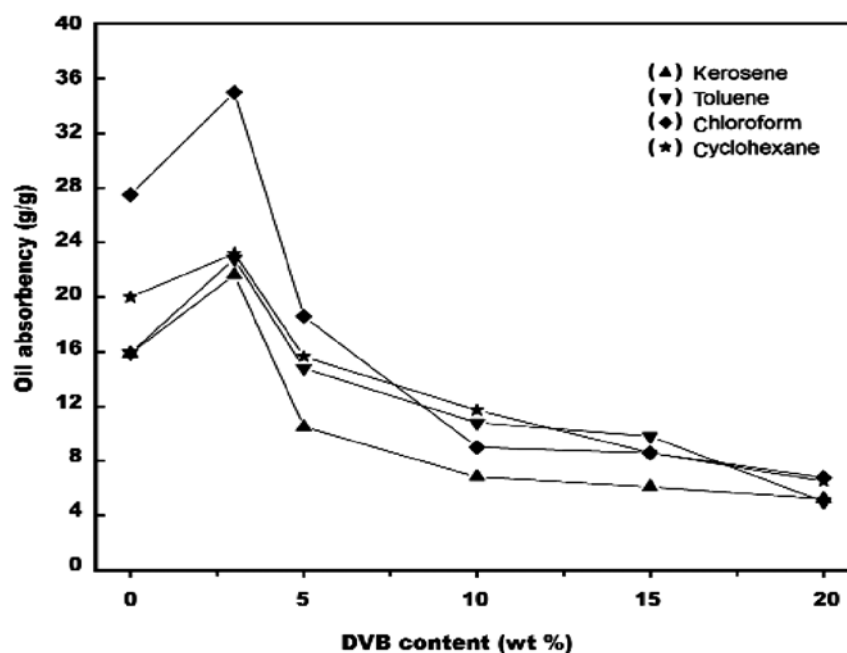


Figure 6. Variation of liquids adsorption with the contents of curatives for a copolymer of DVB-EPDM (DVB-divinylbenzene) in various solvents [27]

Rys. 6. Różnica w stopniu adsorpcji różnych rozpuszczalników przez kopolimer DVB-EPDM (DVB – diwinylobenzen) w zależności od zawartości środka sieciującego [27]

3.9. Effect of fillers

When a crosslinked polymer with different concentration of reinforcing and non-reinforcing fillers is brought into contact with a solvent, the network absorbs a certain amount of liquid to an extent determined also by the filler presence and the polymer-filler interactions. Commonly a decrease in adsorption with increasing filler concentration can occur, because each filler particle behaves as an obstacle to the diffusing liquid. As the concentration of filler increases in the rubber matrix, more and more obstacles are created to the diffusing molecules and thus reduce the amount of penetrating solvent [24, 28].

3.10. Effects of temperature on swelling

3.10.1. Swelling at lower temperature

Most elastomers perform reasonably well at temperatures down to about 40–50 °C, as at such low temperatures the rate of swelling is rather low. Standard seals and especially oil swelling elastomers meant for that purpose become a problem as most oils at low temperatures are quite viscous and the diffusion coefficient causing swell is quite low. Combined with the higher hardness of the elastomer at lower temperatures, the result is a slow swelling at low absolute levels of swelling [26]. Initially, when rubber samples are placed in oil at room temperature, during the first day of exposition a quick penetration of light hydrocarbons can be expected because of washout of plasticizer from the rubber volume. Further, together with the plasticizer elution, material swelling occurs caused by diffusion of higher fractions of the oil into the elastomer [26].

3.10.2. Swelling at higher temperature

Powers and Billmeyer [28] in their investigations found that raising the temperature increases the level of swelling, but the rate of increase was different for various synthetic rubbers, which was caused by changes in composition. At higher temperatures equilibrium is reached earlier than at room temperature. The solvent-absorption speed increases with raising temperature. This can be explained by faster movements of molecules in between the elastomer chains at higher temperatures which speed up the process of swelling, because of increase in diffusion coefficient [29]. It needs to be remembered that raising the temperatures also reduces elastomer strength – it causes a change in dimensions and

loss of physical properties. As described in [28], in most cases the hardness decreases with increasing degree of swelling but for samples at 100 °C there is a noticeable increase. This phenomenon may be due to further curing of the samples under that test condition. The impact of temperature on the absorbency is a swelling equilibrium problem for the three-dimensional network. Many research groups have presented theoretical models, but so far there are no commonly accepted theories. The classical Flory-Rehner equation of Flory's swelling theory does not consider the effect of composition on the interaction parameter and neglects entanglement structures, which are formed by physical crosslinking and indeed more or less exist in a three-dimensional network.

Choi and coworkers [30, 31] extended the Flory-Huggins theory, considering the interaction parameter as a function of both temperature and composition and also the effect of physical crosslinking. However, the presented model may be inaccurate because results obtained by Shan *et al.* [29] deviated to a certain degree from the expected tendency from Choi *et al.* So the swelling equilibrium problem of partially physically crosslinked networks still needs further consideration.

3.11. Impact of swelling on elastomer properties

The more non-organic ingredients are added to a compound for improving properties, the less elastomer remains per unit volume. The elastomer imparts strength to the product, this means that it has to maintain the strength of the whole after swelling, the remaining elastomer has to have increased strength. With higher crosslink density the elastomer is more rigid, it increasingly resists the load created by the fluid and consequently the tendency to swell decreases [8]. Therefore it is crucial to keep a proper balance between swell performance and mechanical integrity for both sealing and pressure containments [8]. Powers and Billmeyer [28] noted, that volatile swelling liquids generally reduce the tensile strength much more for a given amount of swelling than non-volatile oils. It is important to carry out accurate measurements of material responses of the elastomer under given conditions and at various stages of swelling. Success of an elastomer-based field application depends on many factors indeed, such as improvement of sealing design, and assessment of seal integrity, selection of the type of swell packers that are suitable for a given set of field conditions, etc. [3].

In the presence of oil, the fatigue life of an EPDM sample under dynamic multi-axial loading can be significantly reduced, even for relatively small amounts of swelling. The lower fatigue life of the

swollen specimens can be assigned to a number of physical and chemical factors. Physical factors include a lower initial complex modulus following swelling, breakdown of mutual filler-filler bonds and the presence of larger voids in the network because of the swelling action. Chemical factors include changes in the network structure due to swelling, where there is a reduction in the number of chains resisting the tensile force, while the reformation of polysulphidic linkages during a loading cycle can be inhibited in the presence of a swelling fluid.

The general fatigue behavior of swollen elastomers loaded multiaxially is in close agreement with the experiments carried out in uniaxial and shear loading cases [32]. Variation of the fatigue resistance can be observed in an elastomer in the swollen state due to the reduction in viscoelastic energy loss and sharpening of the crack tip when the rubber is swollen [32].

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